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THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research and Advanced Technology Division

United Technology Center

U
A
DIVISION OF UNITED AIRCRAFT CORPORATION

P.O. BOX 358, SUNNYVALE, CALIFORNIA

SEVENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 SEPTEMBER THROUGH 30 NOVEMBER 1962
CONTRACT No. Nonr 3433(00)

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DEPARTMENT OF THE NAVY
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WASHINGTON 25, D. C.

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Propulsion Chemistry Branch
Material Sciences Division
Office of Naval Research
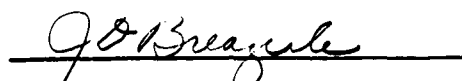
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(This project is financially supported by the
Advanced Research Projects Agency)
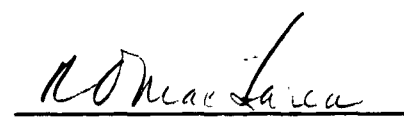
Technical Specialists Actively Engaged in the Project:

C. E. Fogle and R. T. Rewick

Report Prepared by: Report Submitted by:

J. D. Breazeale   R. O. MacLaren
Project Scientist   Project Manager

                                        Report Approved by:

                                        D. D. Ordahl, Manager
                                        Propulsion Research Branch

ABSTRACT

The preliminary value obtained for the heat of formation of fluorine per-chlorate from the heat evolved during fluorination of 70 percent perchloric acid has been refined to yield the value of +18.5 Kcal/mole. However, con-siderable uncertainty is still associated with this value as a result of ex-perimental variations. From preliminary calorimetric studies of the gas phase reaction of fluorine perchlorate with hydrogen, the determination of the heat of combustion appears to be an attractive alternative for the evalu-ation of the heat of formation of fluorine perchlorate.

Mass spectrographic analysis of trifluoromethyl hypofluorite has shown that a purity of greater than 97 percent has been achieved for this material and has established that the technique employed for the removal of COF_2, the primary by-product, is particularly effective. Pentafluorosulfur hypo-fluorite has been purified by repetitive fractional codistillation and is cur-rently being analyzed by mass spectrographic technique.

Fluorine nitrate has been found to be reactive with hydrogen and explosive mixtures have been obtained. The material also hydrolyzes readily in caustic solution under conditions achieved in the modified two-chamber gas combustion bomb. Further modification of the equipment would permit quantitative calorimetric studies to be conducted. However, since a reli-able heat of formation value has been derived for this compound earlier in the program, this approach is being deferred in favor of evaluation of heats of formation of other O-F compounds.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

This report is the Seventh Quarterly Technical Summary Report issued in partial fulfillment of Contract Nonr 3433(00). This report covers the work accomplished during the months of September, October, and November, 1962.

2.0 OBJECTIVES

The objective of the current program is an evaluation of the O-F bond energy in compounds exhibiting well-defined O-F bonding. Previous studies have established the value of the heat of formation of NO_3F to be +2.5 Kcal/mole by measurements involving the synthesis reaction in a flow calorimeter. From this value of the heat of formation, an O-F bond energy of 45 Kcal may be inferred based on reasonable values for the N-O bond energies.

The specific objectives of the research effort conducted during the present report period have been as follows:

A. Measurement of the heat of formation of ClO_4F by direct synthesis in a flow calorimeter

B. Screening of reactions of NO_3F and ClO_4F for suitability for calorimetric determinations of heats of reaction to corroborate heats of formation derived from synthesis reactions

C. Completion of an investigation of purification procedures for CF_3OF, FSO_3F, and F_5SOF and development of procedures for the accurate analysis of reaction products obtained in the synthesis of hypofluorite materials

D. Preparation of high purity NO_2F and evaluation of a more precise value of the heat of formation by determination of the dissociation pressure of this material.

3.0 TECHNICAL ACTIVITY

3.1 STUDY OF NO_3F

Since the results of efforts reported earlier[1] appeared to indicate hydrogen to be unreactive with fluorine nitrate, an investigation of other reactions has been conducted to evaluate their applicability to calorimetric study. The criteria of suitability were: simple, well-defined products with known thermochemical properties; reproducibility; and absence of solid products resulting from gas phase reactions.

Fluorine nitrate has been reported to undergo the following decomposition reaction when sparked in an aluminum apparatus:[2]

$$NO_3F \longrightarrow NOF + O_2 \tag{1}$$

This reaction would appear to meet the requirements and to be ideally suited to calorimetric evaluation. However, a different stoichiometry was found in this laboratory for decomposition of NO_3F in a stainless steel system. By infrared analysis, considerable NO_2 was found in the product gas along with several peaks for unidentified products. In the event that the Al_2F_6 passivation coating on the walls of the aluminum apparatus possessed catalytic activity and influenced the composition of the end products, a small amount of Al_2F_6 was added to the reactor. No difference was noted in the products obtained from the catalyzed and uncatalyzed reactions.

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[1] Breazeale, J., "Thermochemistry of Oxygen-Fluorine Bonding", Quarterly Technical Summary Report No. 5, 2002-QT-5, Contract No. Nonr 3433(00) United Technology Corporation, May 1962.

[2] Cady, G.H., Skiens, W.E., J. American Chemistry Society, 80, 5640, (1958).

The hydrogen combustion calorimeter was modified to permit preliminary studies to be made of the hydrolysis of NO_3F with aqueous NaOH. A stirrer was provided to enhance the gaseous-liquid contact and promote the hydrolysis reaction. The data presented in Table I indicate that a sufficiently high degree of hydrolysis is achieved in a reasonable time accompanied by a marked temperature rise. Hydrolysis studies in slightly refined equipment, therefore, would prove suitable for obtaining calorimetric data for oxygen-fluorine bonded compounds.

TABLE I

HYDROLYSIS OF NO_3F

	Run No.	
	1	2
NO_3F, m moles	2.06	2.10
NaOH, m moles	10.0	10.0
ΔT, $^{\circ}C$	0.34	0.52
NO_3F after hydrolysis, m moles	0.861	0.749
Hydrolysis, percent	58.2	64.3
Reaction Time, minutes	10.5	20.0

Additional attempts were made to initiate a reaction between NO_3F and H_2 by (1) the use of platinum black and (2) 10% palladium on charcoal. Neither experiment gave any indication of a reaction of the NO_3F with the fuel.

The apparent lack of reactivity of NO_3F in a strongly reducing atmosphere of hydrogen was still highly suspect, and the effect of the diffusion characteristics of the two gases on mixing under the experimental conditions was investigated. The initial assumption that only a short time would be required to develop a uniform concentration in the combustion bomb proved to be erroneous. Modification of the experimental technique (i.e., ignition

in the oxidizer chamber rather than in the fuel chamber to take advantage of the greater rate of diffusion of hydrogen as well as the greater pressure normally in the fuel cylinder) resulted in a mixture which exploded upon spark ignition. Apparently the explosion limits for this system are considerably narrower than the oxygen-hydrogen system used to calibrate the calorimeter.

The data for two combustion experiments with NO_3F and hydrogen are presented in Table II. In both cases, the reaction was quite exothermic, and resulted in condensed as well as gaseous products. Approximately one percent of the gaseous material was condensible in a liquid oxygen trap and the remainder was infra-red inactive. In the second experiment, reduction of the exposed surface area of Teflon insulation in the reactor resulted in approximately one-half of the amount of CO_2 and CO found in the first experiment. The poor agreement between the theoretical fluoride and the experimentally observed fluoride content of the aqueous product of the reaction may be attributed, in part, to difficulties in sampling and analysis and possibly to incomplete combustion. It is apparent that explosive mixtures of NO_3F and H_2 can be obtained, although the concentration range is narrower than at first expected. However, combustion reactions with hydrogen may be amenable to calorimetric study not only for NO_3F, but for additional hypofluorites.

TABLE II

REACTION OF NO_3F AND H_2

	Run No.	
	1	2
NO_3F, m moles	2.04	2.06
Pressure H_2 required, psi	63.0	63.0
Pressure H_2 used, psi	84.9	84.7

TABLE II (Continued)

REACTION OF NO_3F AND H_2

	Run No.	
	1	2
Wt., liquid or solid product, gm.	----	0.073
Theoretical F, m moles	----	2.06
Observed F, m moles	----	1.48
Infrared analysis, gaseous product	NO_2, NO_3 CO_2, CO H_2O	NO_2, NO_3 CO_2, CO H_2O
Condensable gaseous product, percent	~2	1

3.2 STUDY OF ClO_4F

3.2.1 Synthesis Calorimeter Experiments

The accuracy of the measurement of the heat released in the synthesis of fluorine perchlorate by the reaction of fluorine with 70 percent perchloric acid in the synthesis calorimeter described previously[3] suffers from the poor heat transfer through the Kel-F walls of the reactor. The long equilibration time, as well as the apparent variation in the rate of heat leakage to the calorimeter, contribute to this uncertainty. The reactor was modified by reducing the thickness of the walls to 1/16 inch, which was approximately one-half of their original thickness. This was done to enhance the heat transfer to the sink fluid. The results of six experiments conducted in this system are given in Table III.

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[3] Breazeale, J., "Thermochemistry of Oxygen-Fluorine Bonding," Quarterly Technical Summary Report No. 6, 2002-QT6, Contract Nonr 3433(00), United Technology Corporation, August 1962.

TABLE III

REACTION OF F_2 AND $HClO_4$ (70%)

	Run No.					
	2	3	4	5	6	7
F_2, m moles	7.64	7.64	6.85	6.32	5.87	6.58
Reaction time, minutes	21.0	25.0	25.0	27.0	23.0	27.0
F_2 flow rate, m moles/minute	0.36	0.31	0.27	0.23	0.25	0.24
ClO_4F, m moles	2.13	~2.43	2.42	2.44	1.87	2.30
Conversion, percent	28.6	----	36.3	39.6	33.2	35.9
C_p, cal/deg	6454	~6454	6487	6566	6704	6646
Calories liberated	64.5	~83.9	71.4	85.4	107.3	73.1
$\Delta H_{f\,298}$, Kcal/mole	+18.7	~+14.4	+19.5	+14.0	-8.4	+17.2
Analysis: Theoretical						
F^-, m moles	----	----	2.14	2.15	1.58	----
ClO_4^-, m moles	----	----	2.14	2.15	1.58	----
H^+, m moles	----	----	4.28	4.30	3.16	----
Observed:						
F^-, m moles	----	----	2.11	2.19	1.79	----
ClO_4^-, m moles	----	----	1.92	1.98	1.50	----
H^+, m moles	----	----	4.10	4.22	3.21	----

Avg. $\Delta H_{f\,298}$ ClO_4F (runs 2, 4, 7,) = +18.5 Kcal/mole

The average value inferred for the heat of formation of fluorine perchlorate based on a selection of experimental values made on statistical considerations was found to be +18.5 Kcal/mole. However, the heat of formation values still retain a considerable degree of uncertainty, owing to both an abated but continued heat transfer problem with a resultant long equilibration period following reaction, and the large heat capacity of the system owing to the large quantity of water required to cover the apparatus. In addition, the slope of the final drift rate period was considerably greater than that of the initial period for a typical run (Figure 1). The data for the initial and final drift rate periods were fitted to straight lines by the method of least squares, and the true temperature rise was determined by subtracting a heat leak correction employing the average slope of the two drift lines from the observed equilibrium temperature rise. The heat leak correction was large compared to the total temperature increase; therefore, the derived heat of formation value is quite sensitive to the value employed for the drift rate. For example, for the data shown in Figure 1, the over-all heat leak correction for the determination of the true temperature rise is 85 percent of the observed value owing to the large equilibration period following reaction, and the derived heat of formation value varies from +9.6 to +27.8 Kcal/mole depending upon the use of either the initial or the final slope rates for applying the heat leak correction. The average heat of formation value of +18.5 Kcal/mole for runs 2, 4, and 7 thus possesses considerable uncertainty.

A smaller Kel-F synthesis calorimeter was designed which would reduce the over-all heat capacity of the system by a factor of 4, resulting in a correspondingly greater rise in temperature and would also result in a shorter equilibration time. However, in preliminary
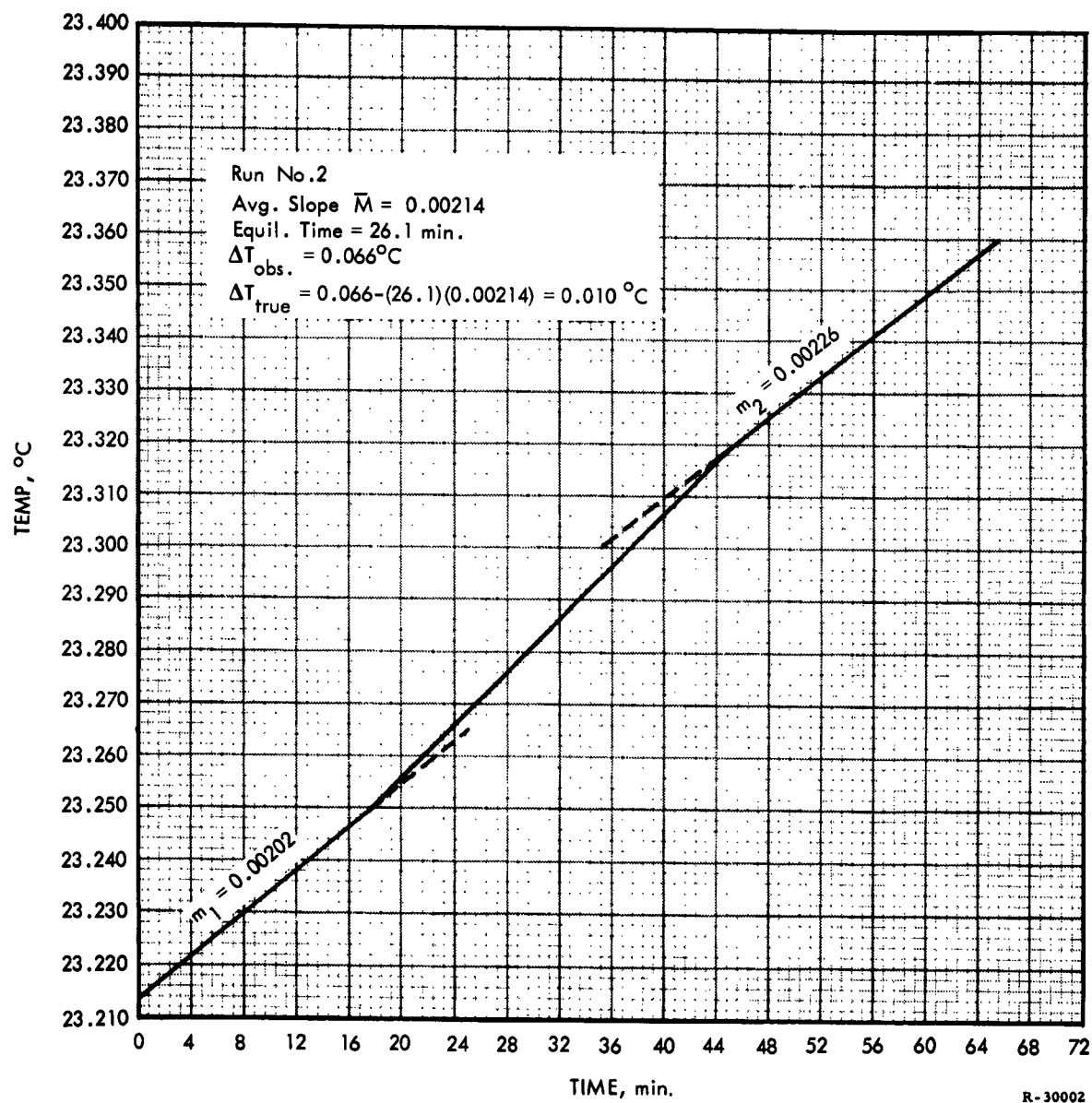
Figure 1. Calorimetric Data: Reaction of F_2 and $HClO_4$ (70 percent)

synthesis check-outs of the apparatus, yields of ClO_4F of approximately 10 percent were realized, presumably a consequence of the 40 percent reduction in the amount of $HClO_4$ contained in the reactor and the resulting shortened fluorine-perchloric acid contact time.

To explore the role of the perchlorate ion (and, indirectly, of any other equilibrium involving perchloric acid in the synthesis of fluorine perchlorate) the fluorination of a solution containing essentially the same perchlorate concentration as contained in the 70 percent $HClO_4$ solution was conducted. The reaction

$$ClO_4^- + F_2 \longrightarrow F^- + ClO_4F \tag{2}$$
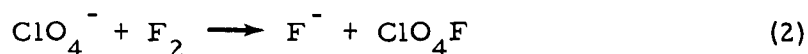
should be exothermic, yielding approximately 24 kcal/mole. Table IV presents the data for two experiments. The low yields which were obtained would suggest that the role of the perchlorate ion in the synthesis of ClO_4F is not significant and further precludes the use of this reaction for calorimetric study.

TABLE IV

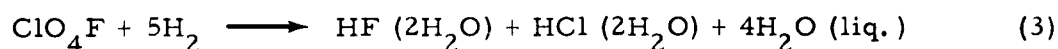REACTION OF F_2 AND $NaClO_4$

	Run No.	
	1	2
F_2, m moles	7.11	9.22
ClO_4^-, m moles	300	300
Reaction time, minutes	15	20
ClO_4F, m moles	0.216	0.287
Yield, percent	3.12	3.19

3.2.2 Combustion Calorimeter Experiments

In previous attempts to produce a reaction between ClO_4F and H_2, inadequate mixing by diffusion appears to be the source of difficulties encountered.[4] Modification of the experimental technique employed in the combustion experiments, which proved effective in the combustion of NO_3F with H_2, resulted in a mixture of ClO_4F and H_2 which could be exploded with the aid of a spark. Infrared analysis of the combustion products of several preliminary experiments indicated the presence of only trace amounts of ClO_4^- on the windows of the infrared cell and several minor peaks of possible Cl-F, Cl-O, and O-F products.

Despite the fact that a small amount of unidentified impurity was present in the ClO_4F reactant, several calorimetric combustion studies were conducted. A typical time-temperature curve of a ClO_4F-H_2 combustion experiment is shown in Figure 2. The variation among the heat of formation values for several combustion experiments shown in Table V and the discrepancy between these figures and those obtained from direct synthesis calorimetry may be a consequence of several factors. The presence of impurities in the fluorine perchlorate will affect the value derived for the heat of formation of the pure material since thermal conductivity measurements indicated the presence of 2-5 percent of extraneous material. Another potential source of considerable error is incomplete combustion or failure of the reaction to proceed as assumed in Equation 3:

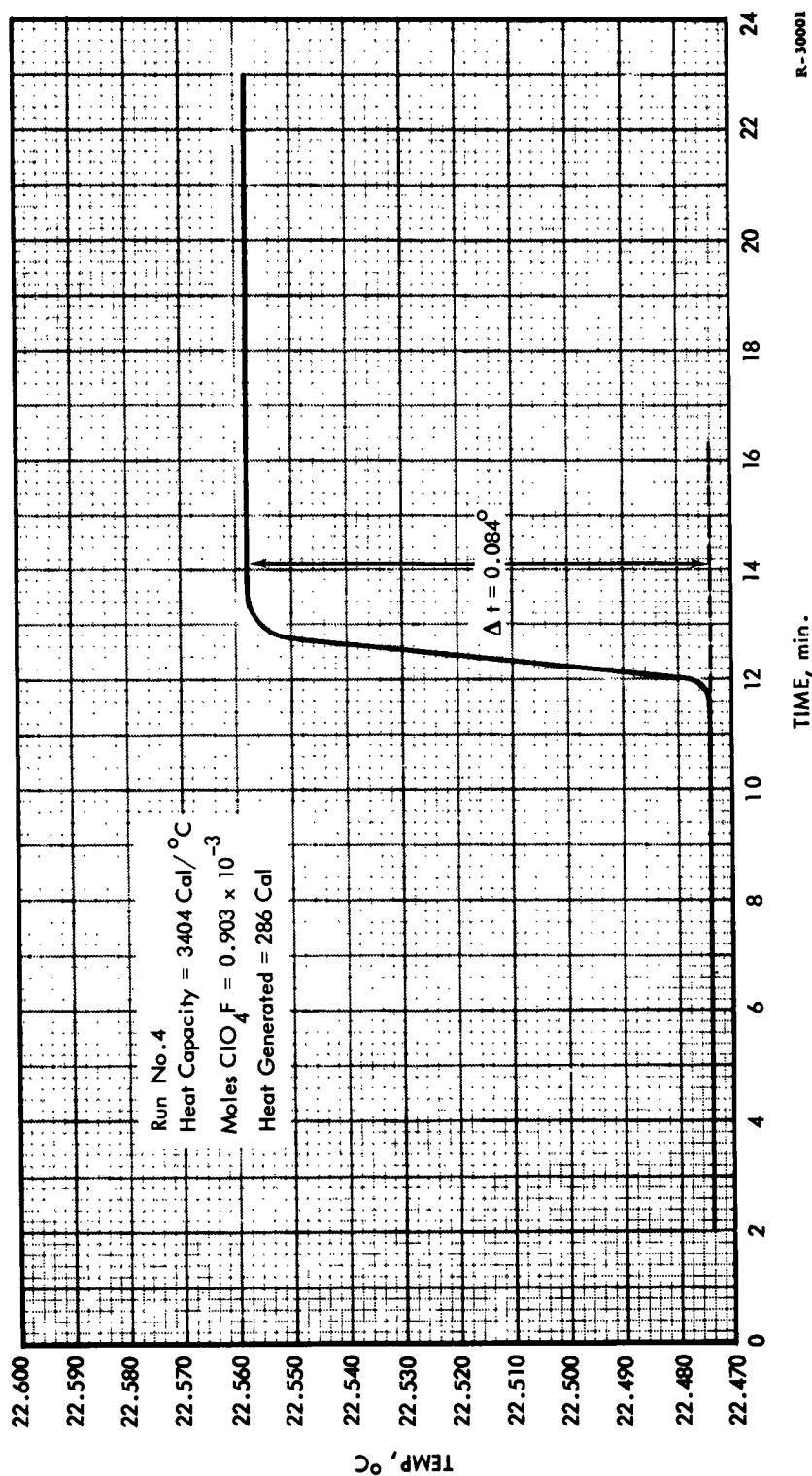$$ClO_4F + 5H_2 \longrightarrow HF\ (2H_2O) + HCl\ (2H_2O) + 4H_2O\ (liq.) \qquad (3)$$

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[4] Ibid

Figure 2. Calorimetric Data: ClO_4F and H_2

Run No.4

Heat Capacity = 3404 Cal/°C

Moles ClO_4F = 0.903 x 10^{-3}

Heat Generated = 286 Cal

$\Delta t = 0.084°$

R-30001

TABLE V

REACTION OF ClO_4F AND H_2

	Run No.			
	1	2	3	4
ClO_4F, m moles	0.725	0.871	0.886	0.903
Pressure H_2 req., psi	32.0	39.0	40.0	40.0
Pressure H_2 used, psi	74.7	79.7	84.7	84.7
C_p, cal/deg.	3518.0	3444.0	3445.0	3404.0
Calories liberated	331.0	282.0	300.0	285.0
ΔH_f 298', Kcal/mole	+78.0	-54.0	-39.0	-61.0
Infrared analysis: ClO_4F:	-	impurities	impurities	impurities
	-	805 cm^{-1}	805 cm^{-1}	805 cm^{-1}, 950 cm^{-1}
	-	1767 cm^{-1}	1767 cm^{-1}	1767 cm^{-1}
Products:	NO_3^-	CO, CO_2	SiF_4	F^-, ClO_4^-
	ClO_4^-	HCl, NO_3^-	F^-	Traces other
	Unidentified Cl-F;	Possible HC $\equiv$ CH		Cl-O compounds
	Possible Cl-O;O-F			
Condensable impurities, percent in product	-	<0.3	-	-

3.3 STUDY OF CF$_3$OF

A quantity of CF$_3$OF has been prepared whose infrared spectrum was entirely free of COF$_2$ absorption peaks. Since analyses of hydrolyzed samples of this material have varied considerably from the theoretical values, samples were also submitted for mass spectrographic analysis. In this manner, the results of the three methods of analysis could be compared, yielding a more reliable indication of the purity of the CF$_3$OF.

The mass spectrographic analyses produced the following results:

TABLE VI

MASS SPECTROGRAPHIC ANALYSES OF CF$_3$OF

| Constituent	Sample I Mole Percent	Sample II Mole Percent
CF$_3$OF	97.3+	97.4+
CO$_2$	1.1	1.3
HF	1.2	0.8
O$_2$	0.3	0.4

Carbonyl fluoride, the major by-product of the synthesis of CF$_3$OF, was not found, which corroborates the infrared analysis.

The mass spectrographic analyses have been converted into elemental carbon and fluorine percentages for comparison with the results from the chemical hydrolysis of the same material. Comparison of the results indicates that the fluorine content determined from hydrolysis is slightly low.

TABLE VII

COMPARISON OF ANALYSES OF CF_3OF

Method	Carbon Wt. Percent	Fluorine Wt. Percent
Theoretical	11.5	73.1
Chemical Hydrolysis	11.8	70.8
		70.4
Mass Spectograph		
Sample I	11.5	72.3
Sample II	11.6	72.0

Experiments performed in this laboratory and by Cady[5] indicate that CF_3OF and H_2 do not react at ambient temperatures; therefore several additional reactions were investigated in an attempt to obtain thermochemical data to corroborate data obtained for CF_3OF by high temperature vapor phase dissociation.[6] Trifluoromethyl hypofluorite has been reported[6] to react quantitatively with mercury and semi-quantitatively with sulfur according to Equations 4 and 5 :

$$CF_3OF + 2\ Hg \longrightarrow COF_2 + Hg_2F_2 \qquad (4)$$

$$16\ CF_3OF + S_8 \longrightarrow 16\ COF_2 + 8\ SF_4 \qquad (5)$$
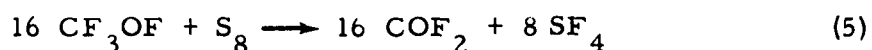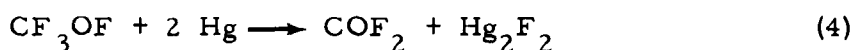
CF_3OF was reported to be maintained in contact with mercury with constant agitation for an extended period. These conditions are not directly amenable to calorimetric study. The characteristics of the reactions in a flow system were investigated to establish possible applicability to calorimetric study. However, although some evidence of reaction was detected, the reaction did not proceed at a sufficient rate for further use.

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[5] Cady, G.H., J. American Chemistry Society, 70, 3986, (1948).

[6] Cady, G.H. and R.S. Porter, J. American Chemistry Society, 79, 5628, (1957).

The original report of the reaction of CF_3OF with sulfur indicated a third unidentified product which was obtained in low yields and which decomposed at room temperature. The results of current studies suggest that a complex mixture of products is obtained from the reaction and that a different stoichiometry is involved. A relatively large concentration of unidentified products renders this reaction unsuitable for calorimetric application.

3.4 STUDY OF F_5SOF

Work has continued on the further purification of F_5SOF. Progress has been made by further refining the fractional codistillation apparatus. The use of 30-60 mesh Kel-F packing has been particularly effective. Successive distillation of the material with this column has reduced the several impurity peaks to the detection limit of the thermoconductivity apparatus. The one remaining impurity peak has an area of 0.5 percent of the total product peak area. Infrared analysis of this material, however, indicates the presence of some SO_2F_2 and SOF_4. A sample has been submitted for quantitative analysis by mass spectrographic techniques.

3.5 STUDY OF NO_2F

Work has been initiated to explore the feasibility of obtaining the heat of dissociation of NO_2F according to the reaction,

$$NO_2F \longrightarrow NO_2 + 1/2\ F_2 \tag{6}$$
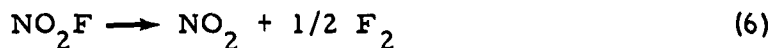
At room temperature, an apparent equilibrium exists between F_2, NO_2, and NO_2F. This is visually evidenced by the disappearance of the red-brown color of NO_2 when an excess of fluorine is added to NO_2F and its reappearance when the excess fluorine is removed. Equipment has been assembled which will be employed in measuring the dissociation pressure of the reaction in Equation 6.

4.0 FUTURE WORK

To establish a more reliable value for the heat of formation of fluorine perchlorate, additional studies will be conducted to measure the heat of combustion of fluorine perchlorate with hydrogen. Sufficiently promising results have been obtained to warrant the pursuit of this approach for direct calorimetric evaluation.

The high temperature synthesis reactions of trifluoromethyl hypofluorite, fluorine fluorosulfonate, and pentafluorosulfur hypofluorite are not readily adapted to calorimetric study. Therefore, the hydrolysis reactions will be evaluated for their applicability.

Experiments will also be conducted to establish a more precise value for the heat of formation of nitryl fluoride from a study of its equilibrium dissociation reaction as a function of temperature.